10/532132 #2

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Sertifikaat

Certificate

REPUBLIEK VAN SUID AFRIKA

PATENT KANTOOR
DEPARTEMENT VAN HANDEL
EN NYWERHEID

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE
DEPARTMENT OF TRADE AND
INDUSTRY

Hiermee word gesertifiseer dat
This is to certify that

1) South African Patent Application No. **2003/2919** accompanied by a Provisional specification was filed at the South African Patent Office on **11 April 2003** in the name of **Sasol Technology (Pty) Ltd** in respect of an invention entitled: **" Process for preparing esters or carboxylic acids "**

2) The photocopy attached hereto is a true copy of the provisional specification filed with South African Patent Application No. **2003/2919.**

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Gedateer te **PRETORIA** in die Republiek van Suid-Afrika, hierdie **20th** dag van **April** **2004**

Dated at in the Republic of South Africa, this day of

.....
Registrar of Patents

Form P.2

REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

REGISTER OF PATENTS

OFFICIAL APPLICATION NO.	LODGING DATE : PROVISIONAL	ACCEPTANCE DATE
21 2003/2913	22 11 April 2003	43
INTERNATIONAL CLASSIFICATION	**LODGING DATE : COMPLETE**	**GRANTED DATE**
51	23	

FULL NAME(S) OF APPLICANT(S) / PATENTEE(S)

71 SASOL TECHNOLOGY (PTY) LTD

APPLICANTS SUBSTITUTED :	DATE REGISTERED
71	

ASSIGNEE(S)	DATE REGISTERED
71	

FULL NAME(S) OF INVENTOR(S)

72 GREEN, Michael James

CROUS, Renier

PRIORITY CLAIMED	COUNTRY	NUMBER	DATE
N.B. Use international abbreviation for country. (See Schedule 4)	33	31	32

TITLE OF INVENTION

54 PROCESS FOR PREPARING ESTERS OR CARBOXYLIC ACIDS

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REF P26579ZA00

PATENT OF ADDITION NO.	DATE OF ANY CHANGE
61	

FRESH APPLICATION BASED ON	DATE OF ANY CHANGE

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

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REPUBLIEK VAN SUID-AFRIKA

PBHR 229

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT
(Section 30 (1) - Regulation 22)
The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate.

OFFICIAL APPLICATION NO	DMK REFERENCE
21 01 2003/2919	P26579ZA00

FULL NAME(S) OF APPLICANT(S)

71 SASOL TECHNOLOGY (PTY) LTD

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TITLE OF INVENTION

54 PROCESS FOR PREPARING ESTERS OR CARBOXYLIC ACIDS

THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANING FORM P2
The earliest priority claimed is

THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.	21	01	
THIS APPLICATION IS FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON APPLICATION NO.	21	01	

THIS APPLICATION IS ACCOMPANIED BY :

x	1a	A single copy of a provisional specification of 14 pages.
	1b	Two copies of a complete specification of pages.
	2a	Informal drawings of sheets.
	2b	Formal drawings of sheets.
	3	Publication particulars and abstract (form P8 in duplicate).
	4	A copy of figure of the drawings for the abstract.
	5	Assignment of invention (from the inventors) or other evidence of title.
	6	Certified priority document(s).
	7	Translation of priority document(s).
	8	Assignment of priority rights.
	9	A copy of form P2 and a specification of S.A. Patent Application. 21 01
	10	A declaration and power of attorney on form P3.
	11	Request for ante-dating on form P4.
	12	Request for classification on form P9.
	13a	Request for delay of acceptance on form P4.
	13b	

DATED 11 April 2003

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REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

PROVISIONAL SPECIFICATION

(Section 30 (1) - Regulation 27)

OFFICIAL APPLICATION NO.	LODGING DATE	DMK REFERENCE
21 2003/2919	22 11 April 2003	P26579ZA00

FULL NAME(S) OF APPLICANT(S)	
71	SASOL TECHNOLOGY (PTY) LTD

FULL NAME(S) OF INVENTOR(S)	
72	GREEN, Michael James CROUS, Renier

TITLE OF INVENTION	
54	PROCESS FOR PREPARING ESTERS OR CARBOXYLIC ACIDS

TECHNICAL FIELD

This invention relates to a process for preparing esters or carboxylic acids from olefins, carbon monoxide, a source of hydroxyl and a palladium catalyst.

BACKGROUND ART

The reaction of olefins, carbon monoxide, and alcohol in the presence of a Group VIII metal catalyst to form esters (also known as a hydroesterification reaction) is well known. The final product of the reaction is reliant on the source of hydroxyl groups that is used. The use of water gives rise to the corresponding carboxylic acid whereas the use of an alkanol leads to the corresponding ester. The catalyst system typically used in hydroesterification reactions preferably comprise a halide free palladium source, a triorganophosphine (could be mono- or bidentate) and a source of anions. It is believed that the size of the anion and the distribution of electric charge in the anion significantly contribute to the stability of the catalyst system. Suitably, acids are used as the source of anions. Preferably, anions are used that are the conjugated base of acids having a pKa (measured at 18°C in water) of less than three. One of the most important functions of these anions are to provide an essentially non-coordinating or weakly coordinating anion to the palladium center, thereby creating a highly active catalytic system (see EP 235 864 A1).

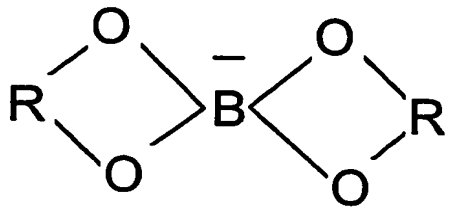
A major drawback in hydroesterfication reactions is the unwanted side reaction

of the acid promoter (that is the source of the anion) with the alcohol (most notably with methanol as reagent) leading to a fraction of the acid being esterified. It is believed that the product of this side reaction can act as a potent alkylating agent which subsequently reacts with the free triorganophosphine ligands in solution to form inactive phosphonium salts of the ligands. In this manner, substantial amounts of the anion and ligand are lost from the reaction medium. This leads to lower catalyst activity, and with time to loss of the palladium metal due to plating.

In order to overcome this problem bulky bidentate ligands (WO 94/18154 and WO95/15938) have been used for the palladium catalyst to provide catalytic systems with improved activity and stability. Compared to monodentate ligands (e.g. triphenyl phosphine), the bidentate ligands need only be present in low concentrations in the reaction medium and thus the likelihood of reaction between the ligand and the acid is lessened to some extent. The bidentate ligands, for example those disclosed in the above two documents, are relatively expensive to produce on commercial scale compared to a monodentate ligand like triphenyl phosphine.

In another attempt to solve the problem (WO 97/03943) weaker carboxylic acids like propionic acid have been used as the source of the anion. Lesser amounts of salts derived from the ligands formed over time, but it was at the expense of catalyst activity.

EP 039 6268, EP 039 1579, EP 031 5318 and EP 031 4309 relate to the preparation of polyketones from olefins and carbon monoxide in the presence of a palladium catalyst. The patents also disclose the addition of a source of anion having a general formula (I):



..... (I)

wherein R is an organic group as defined in that patent.

The inventors have now found that if acids with an anion of the above formula (I) are used instead of the known acid promoters (like methanesulphonic acid) in hydroesterifcation reactions, the problem of the formation of inactive salts of the free ligand is at least reduced. The anions tested were still able to activate the palladium catalyst to form a cationic complex with relatively high catalyst activity but at the same time their conjugate acids were substantially inert to any interactions with the alcohols used. No indication of this advantage is given in the prior art and the results were most unexpected. Not only was the prior art silent on this aspect, but it has to be taken into account that in the prior art reactions for the formation of polyketones (wherein the anions of formula (I) were disclosed), specific bidentate ligands were used as is required for the formation of polyketones. As set out above, in cases where particular bidentate

ligands are used, the formation of inactive salts of the free ligand is not problematic or is at least reduced. In the prior art reactions for the formation of polyketones, alcohols may have been included as solvents, but were not seen as essential for the reaction to occur.

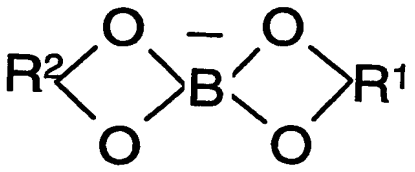
DISCLOSURE OF THE INVENTION

According to the present invention there is provided a process for preparing esters or carboxylic acids by reacting at least one olefin; carbon monoxide; and a source of hydroxyl in the presence of a Group VIII B metal catalyst wherein the palladium catalyst is prepared by the reaction of

i) a source of Group VIII B metal,

ii) an organophosphine, organoarsine or organostibine compound that can act as ligand to coordinate to the palladium, and

iii) an anion or a source thereof of general formula (II)

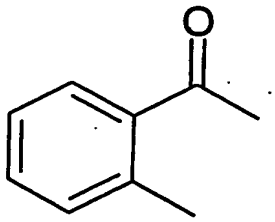


..... (II)

wherein R^1 and R^2 are the same or different and each comprises an organic group.

In a preferred embodiment of the invention at least one of, but preferably both

In a preferred embodiment of the invention at least one of, but preferably both of R^1 and R^2 comprise an aromatic compound. In a preferred embodiment of the invention R^1 and R^2 may independently comprise a compound selected from the group consisting of C_1 to C_6 alkylene; ortho-phenylene or biphenylene; a moiety of the general formula (III)

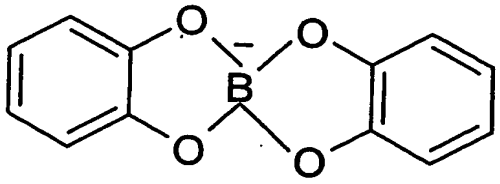


..... (III);

and a substituted derivative of any one of said compounds.

Preferably R^1 and R^2 are the same.

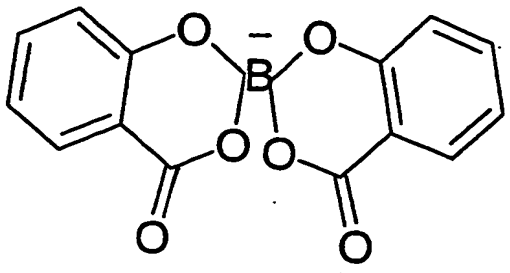
In one embodiment of the invention the anion may comprise the compound (IV)



..... (IV)

or a substituted derivative thereof.

In another embodiment of the invention the anion may comprise the compound (V)



..... (V)

or a substituted derivative thereof.

Preferably the source of the anion is the conjugate acid of the anion.

In one embodiment of the invention the anion or source thereof may be prepared *in situ*. It may be prepared by a condensation reaction between boric acid and a suitable precursor of R^1 and R^2. In the case of compound (IV) the precursor of R^1 and R^2 may be catechol. In the case of compound (V) the precursor of R^1 and R^2 may be salicylic acid.

In another embodiment of the invention the source of the anion may be pre-prepared.

It will be appreciated that the reaction conditions will be selected in order that esters or carboxylic acids form instead of polyketones. These suitable reaction conditions are well known in the art and may include the use of a monodentate ligand like triphenyl phosphine; a bidentate ligand like 1,3-bis(di-tert-butylphosphino)propane, or combinations of one or more of these.

In one embodiment of the invention the process may be for preparing carboxylic acids, in which case the source of hydroxyl may comprise water.

In a preferred embodiment of the invention the process may be for preparing esters in which case the source of hydroxyl comprises an alcohol. In such cases the reaction is known as a hydroesterfication reaction. It is foreseen that any suitable alcohol may be used such as methanol, ethanol, propanol, a diol, a polyhydric alcohol and a phenol, but preferably it comprises methanol.

The ester preferably comprises an aliphatic ester. The ester may comprise a non-branched product and in one preferred embodiment of the invention it comprises methyl propionate. In one preferred embodiment of the invention the process comprises a process for the preparation of methyl propionate wherein the olefin comprises ethylene and the alcohol comprises methanol.

The at least one olefin may comprise a non-functionalised olefin, but it may also comprise an olefin containing one or more functional groups e.g. an ester, a nitrile, an alcohol, an ether, and an acetal.

The at least one olefin preferably comprises only one olefin. The olefin may comprise an α-olefin and preferably it comprises ethylene.

The carbon monoxide may be from any suitable source of carbon monoxide.

The Group VIII B metal catalyst preferably comprises a palladium catalyst which may be fully pre-prepared or partly pre-prepared. For example it is foreseen that a source of palladium may be separately reacted with the ligand to provide a partly pre-prepared catalyst, which is further reacted *in situ* to prepare the catalyst.

In a preferred embodiment of the invention the palladium catalyst is prepared *in situ*.

It is foreseen that any suitable halide free source of palladium may be used such as salts (organic or inorganic) of palladium e.g. carboxylates and nitrates. In one embodiment of the invention the source of palladium may comprise palladium acetate.

Although it is foreseen that bidentate ligands may be used, in the preferred embodiment of the invention the ligand comprises a monodentate ligand. The ligand may comprise a compound with a group VA cental atom for example organophosphine, organoarsine and organostibine. Preferably the ligand comprises an organophosphine. In one embodiment of the invention it comprises a compound of general formula (VI)

$$P(R^3\ R^4\ R^5) \text{ ---------- (VI)}$$

wherein R^3, R^4 and R^5 are the same or different and are independently organyl

groups

In one embodiment of the invention ligand comprises PPh_3.

The reaction is preferably carried out in a solvent. The solvent may comprise the alcohol, but another solvent may also be used, especially where water is the source of hydroxyl.

The quantity in which the catalyst system is used, is usually not critical and may vary within wide limits. For the preparation of the catalyst systems of the invention, the amount of ligand is generally applied in some excess of the amount of the Group VIII B metal cation, expressed as moles of ligand per mole atom of Group VIII B cation. Typically the amount of ligand is selected such that per mole atom of the metal cation (preferably palladium), in the range of from 1.5 – 100 moles of ligand are present. The amount of the anion source may range from 1 – 100 moles per mole of metal cation.

The invention will now be further described by means of the following non-limiting examples:

Example 1

A 300ml Hasteloy C autoclave was loaded with 150ml methanol, 0.0317g $Pd(OAc)_2$ (0.9 mM), the appropriate amount of PPh_3 and the appropriate amount of acid (source of anion) (see Table 1 below). Pressure testing followed

with N_2 at 80 bar after which the reactor was flushed with 10,5 bar C_2H_4 and slowly vented. The reactor was then heated to 100°C over a period of 20 min. while stirring at 1100 rpm. Once the temperature had stabilised the reactor was pressurised with a 1:1 mixture of CO/C_2H_4 up to a total pressure of 30 barg. The gas feed was then switched to a 1L ballast vessel (same gas mixture) and reaction progress was followed *via* pressure drop in the ballast vessel.

Table 1

Acid promoter	**Actual amount**	**[Acid]**	**[PPh_3]**
Borosalicylic acid (preformed)	5.1437 g	0.23M	0.07M
Borosalicylic acid (*in situ*)		0.23M	0.07M
Boric acid	0.9270g	0.20M	0.07M
Salicylic acid	4.1430g	0.10M	0.07M

GC-method

GC analyses were performed on a Shimadzu GC-17A model gas chromatographic unit linked to a PC equipped with Class-VP software for recording and integration of chromatograms. A 30-meter DB-624 column of 0.32 mm internal diameter and 1.8 µm film thickness and a 50-meter Pona column of 0.2mm internal diameter and 0.5 µm film thickness was utilized. A flame ionization detector (FID) was used for detection of reaction components with nitrogen as the carrier gas. Operating conditions for the GC are provided in Table 2:

Table 2

Operational parameter	Condition for DB-624 column	Condition for Pona column
Carrier gas (CG)	Nitrogen	Nitrogen
Column flow	0.9 ml/min	75 ml/min
Initial temperature	35 °C	40 °C
Initial wait	5 min	5 min
Rate	15 °C/min	8 °C/min
Final temperature	250 °C	230 °C
Final time	10 min	5 min
Injector temperature	230 °C	250 °C
Detector temperature	250 °C	280 °C

NMR-experimental procedure

^{31}P-NMR was used to study methyl phosphonium cation formation as a function of time and temperature. In a typical experiment, 5.545g PPh_3 (0.14 M) was suspended in 150 ml methanol (degassed beforehand with argon) in a round-bottom flask. The appropriate amount of acid (source of anion) was then added to afford a total acid concentration of 0.23M. The suspension was stirred vigorously for approx. 40 min. at room temperature until all the ligand had dissolved. In some cases the flask was put into a sonicator to speed up dissolution of the ligand. A 2ml sample of this solution was introduced into the HP-NMR tube along with 1ml of CD_3OD, flushed with argon and sealed. A ^{31}P-NMR-spectrum was recorded immediately at 30°C, then the sample was heated to 90°C and spectra were recorded at regular intervals for approximately 3

hours.

RESULTS

Catalyst activity was calculated using the section of linear gas consumption in each run. Turnover Frequency (TOF) is expressed as moles of methyl propionate formed per mole of palladium per hour. Space Time Yield (STY) is expressed as moles of methyl propionate formed per liter reactor content per hour. The rate of methyl phosphonium salt formation was calculated by comparing the integration in ^{31}P-NMR spectra of the free PPh_3 resonance (δ -4.01 ppm) with that of the methyl triphenylphosphonium cation (δ 22.66 ppm). The borosalicylic acid can be prepared in situ by adding of two equivalents of salicylic acid to one equivalent of boric acid or with the pre-formed method by refluxing the appropriate amounts of salicylic acid and boric acid in benzene and removing water with a Dean-Stark apparatus.

Table 3 : Results

Acid promoter	TOF	STY	S*	Salt formation**
Boric acid	No reaction	0	0	0
Salicylic acid	No reaction	0	0	0
Borosalicylic acid (*in situ*)	476 h^{-1}	0.4	90%	0 % h^{-1}
Borosalicylic acid (prep. separately)	152 h^{-1}	0.15	96%	0% h^{-1}

* S = Selectivity to methyl propionate

** % of total PPh_3 converted to methyl phosponium salt per hour

Comparative Example 2

The NMR procedure described previously was repeated but using methanesulphonic acid instead of borosalicylic acid. A ^{31}P-NMR-spectrum was recorded immediately at 30°C, indicating the formation of trace amounts of the methyl triphenylphosphonium salt. Upon heating the sample to 90°C, there was a rapid increase in the formation of the phosphonium salt. After 1 hour 19% of the total triphenylphosphine inventory was converted into methyl triphenylphosphonium sulphonate.

It will be appreciated that many variations in detail are possible without thereby departing from the spirit of the invention.

Dated this 11 day of April 2003

Patent Attorney / Agent for the Applicant